Molecular photoionization as a probe of vibrational–rotational–electronic correlations

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Molecular photoionization as a probe of vibrational–rotational–electronic correlations

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We determine the rotationally state-resolved $2\sigma_u^{-1}$ photoionization of N_2 into alternative vibrational channels as a function of energy over a 200 eV range. Experiment and theory reveal that Cooper minima highlight the coupling between electronic, vibrational, and rotational degrees of freedom over this very wide range. © *1996 American Institute of Physics.* [S0021-9606(96)03023-1]

Studies of photoion vibrational and rotational distributions provide valuable insights into microscopic aspects of molecular photoionization dynamics.[1–13] Vibrationally resolved spectra probe correlations between photoelectron motion and molecular geometry,[1–4] while rotationally resolved data elucidate the coupling of angular momenta between the continuum electron and the ion core.[5–10,12,13] Our group has recently performed both types of measurements over an extremely broad range,[11–13] emphasizing that molecular aspects of the photoejection process extend far (i.e., >200 eV) into the ionization continuum. These vibrationally resolved studies of N_2 $2\sigma_u^{-1}$ photoionization showed that Cooper minima can lead to non-Franck–Condon behavior over a broad energy range.[11] We have also studied the evolution of the $N_2^+(B\ ^2\Sigma_u^+,\ v^+=0)$ rotational distributions with photoelectron energy, and identified the strong influence of Cooper minima on angular momentum partitioning between the photoelectron and the photoion.[12,13] In this Communication, we report the first study which combines these previous two types of investigations — specifically, by resolving ionic rotation for alternative vibrational levels over a wide energy range. We present both experimental and theoretical results on $N_2^+(B\ ^2\Sigma_u^+)$ rotational distributions for $v^+=0$ and $v^+=1$ following N_2 $2\sigma_u^{-1}$ photoionization in the region $25 \leqslant h\nu_{\mathrm{exc}} \leqslant 210$ eV. By contrasting the rotational distributions for alternative photoion vibrational levels, we investigate fundamental aspects of the dynamics of coupling between electronic and nuclear motion. By simultaneously determining the vibrational and rotational energy deposition into the photoion, this study is the first investigation of its type into vibrational–rotational–electronic (V–R–E) coupling over a broad range of electron energy.

The previous N_2 $2\sigma_u^{-1}$ studies[11–13] and the present investigation cover a range which includes two Cooper minima, and the dominant effects that we observe result from these minima. The present study provides further progress in understanding general aspects of molecular Cooper minima, which are not as fully characterized as those for atomic systems.[14] A Cooper minimum occurs when a principal-value partial wave component of the photoionization matrix element changes sign.[14] This results in a minimum or an inflection point in the cross-section, and an oscillation in the photoelectron asymmetry factor (β). Molecular Cooper minima have been investigated previously.[11–13,15–17] The minimum must occur in a dominant channel if it is to have an appreciable effect on the integrated cross section. While the effects of Cooper minima on photoelectron angular distributions have been studied in detail,[14] their significance for ion vibrational and rotational motions is only beginning to be unraveled. This is because such studies of Cooper minima frequently require broad spectral coverage,[19] which is difficult to achieve with photoelectron spectroscopy. While both REMPI/PES[8,9,16,17] and ZEKE/PFI[5,7,18] studies have generated rotationally resolved photoelectron results, these methods are limited to near-threshold or threshold studies, respectively.

Our experimental technique of detecting dispersed fluorescence from excited photoions[12] circumvents resolving power limitations of photoelectron spectroscopy. When the photoion is created in an excited state, it can either fragment[20] or fluoresce.[21] By dispersing the fluorescence, the detection bandwidth in such an experiment is decoupled from the excitation bandwidth. This enables us to obtain highly resolved data on the photoions while exploiting the broad tunability of synchrotron radiation. Our previous experiments employing dispersed fluorescence to compare the photoion rotational distributions for N_2 and CO demonstrated that the N_2 $2\sigma_u^{-1}$ distributions begin changing rapidly above $h\nu_{\mathrm{exc}} \approx 100$ eV due to the presence of pronounced Cooper minima in the $l=2$ and 4 partial waves of the $2\sigma_u \rightarrow k\sigma_g$ channel. In more recent measurements of N_2 $2\sigma_u^{-1}$ photoion *vibrational* distributions, we have shown that the *R*-dependence of the Cooper minima results in the breakdown of the Franck–Condon approximation over the broadest energy range observed to date.[11] In this Communication, our experiments and calculations show that the same

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R-dependent Cooper minima that lead to non-Franck–Condon ion vibrational distributions also result in different trends in ion rotational distributions for alternative photoion vibrational levels.

The experimental method is described elsewhere.[12,21] Briefly, nitrogen molecules are photoionized, and the fluorescence from the excited photoions is collected, dispersed, and detected. The excitation-fluorescence sequence is the same as that used previously,[11–13] only this time we detect rotationally resolved fluorescence from both $v^+=0$ and $v^+=1$ simultaneously.

$$\begin{aligned} &\mathrm{N}_2(X\ ^1\Sigma_g^+,\ v_0=0,\{N_0\})+h\nu_{\mathrm{exc}} \\ &\quad\rightarrow \mathrm{N}_2^+(B\ ^2\Sigma_u^+,v^+,N^+)+e^- \\ &\qquad\downarrow \\ &\qquad \mathrm{N}_2^+(X\ ^2\Sigma_g^+,v'',N'')+h\nu_{v^+v''N^+N''}. \end{aligned} \tag{1}$$

The N_2 gas is introduced into the interaction region via a free-jet supersonic expansion to limit the number of target rotational states. We estimate the rotational temperature of the N_2 target molecules to be 20 K, using comparisons with theory as described previously.[12] The rotationally cooled target molecules are ionized by monochromatized light ($\Delta h\nu_{\mathrm{exc}} \approx 0.5$ eV) from the Louisiana State University synchrotron radiation source at the Center for Advanced Microstructures and Devices (CAMD).[22] The fluorescence is collected and dispersed, and detected by a CCD optical multichannel analyzer [Princeton Instruments #LN/CCD-1024-EUV]. A comprehensive discussion of the experimental details will be given elsewhere.[23] Pictured in Fig. 1 is one snapshot of a rotationally resolved fluorescence spectrum from the $v^+=0$ and $v^+=1$ vibrational levels of the $N_2^+(B\ ^2\Sigma_u^+)$ state. From such spectra, we extract the relative rotational populations for each vibrational level, as described previously.[12]

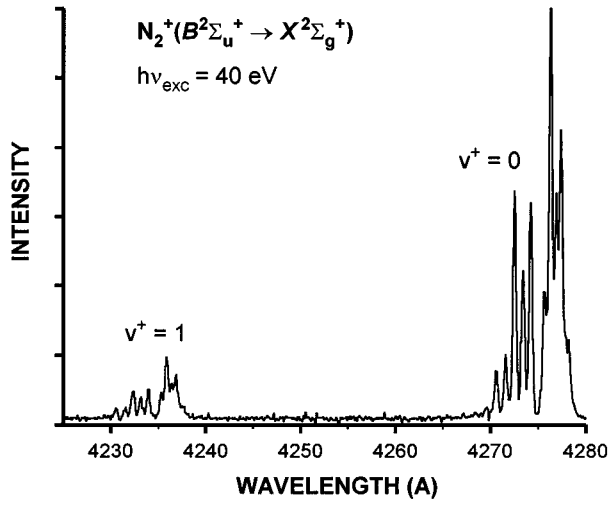

FIG. 1. Rotationally resolved fluorescence spectrum $N_2^+(B\ ^2\Sigma_u^+ \rightarrow X\ ^2\Sigma_g^+)$ showing transitions originating from $v^+=0$ and $v^+=1$ vibrational levels ($v''=1$ and 2, respectively).

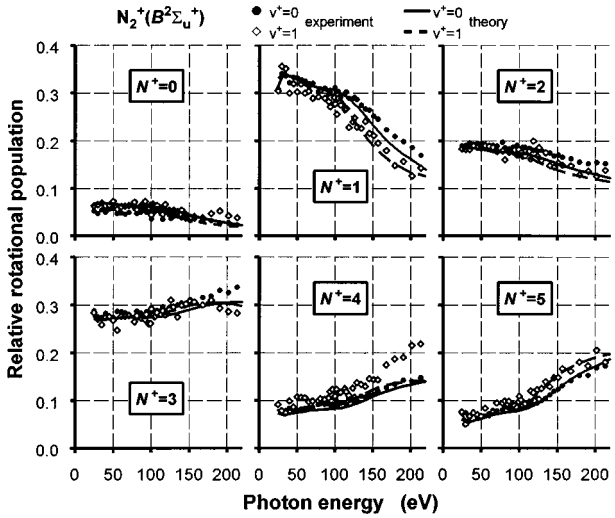

FIG. 2. Relative rotational populations of $N_2^+(B\ ^2\Sigma_u^+)$ state $v^+=0$ and $v^+=1$ vibrational levels. Experimental values determined from spectra such as those in Fig. 1.

The computational procedure used here has been discussed previously.[24] To obtain the photoelectron orbitals, we use an iterative procedure based on the Schwinger variational principle to solve the Lippmann–Schwinger equation.[24] Calculations are performed at the Hartree–Fock frozen-core level, which is sufficient to characterize the key dynamical aspects. The ground state wave function of N_2 is obtained at the self-consistent-field (SCF) level. A single-center expansion around the center of mass shows the $2\sigma_u$ orbital to have 90.65%p, 6.66%f, and 1.52%h character at the equilibrium internuclear distance of $R_e=2.0743$ a.u. This orbital composition changes slowly from 96.86%p and 2.62%f character at an internuclear distance of 1.25 a.u. to 81.52%p and 11.30%f character at $R=3.5$ a.u. Note that the angular momentum composition of the target molecular orbital does not change a great deal over this large range of internuclear separation. This feature is significant for the analysis of the results discussed later.

Fluorescence spectra are obtained for photon energies from $25 \leqslant h\nu_{\mathbf{exc}} \leqslant 210$ eV. The energy-dependence of the rotational populations for $v^+=0$ and $v^+=1$ is compared in Fig. 2. The calculated rotational populations, also shown in Fig. 2, are in good qualitative agreement with experiment. Figure 3 shows the results for two selected levels, $N^+=1$ and $N^+=5$, where the agreement is best in order to emphasize the trends that are observed, as well as to highlight more subtle details. In the lower rotational levels (especially $N^+=1$ and 2), both experiment and theory show a consistently higher population for $v^+=0$ than for $v^+=1$. On the other hand, the higher rotational levels ($N^+=4$ and 5) show a lower population for $v^+=0$ than for $v^+=1$. The intermediate behavior of the $N^+=3$ level is reflected in both theory and experiment, where the $v^+=0$ population is slightly lower at photon energies below 175 eV and overtakes that of $v^+=1$ at higher photon energies. There is a significant discrepancy between the calculated and measured $N^+=4$ popu-

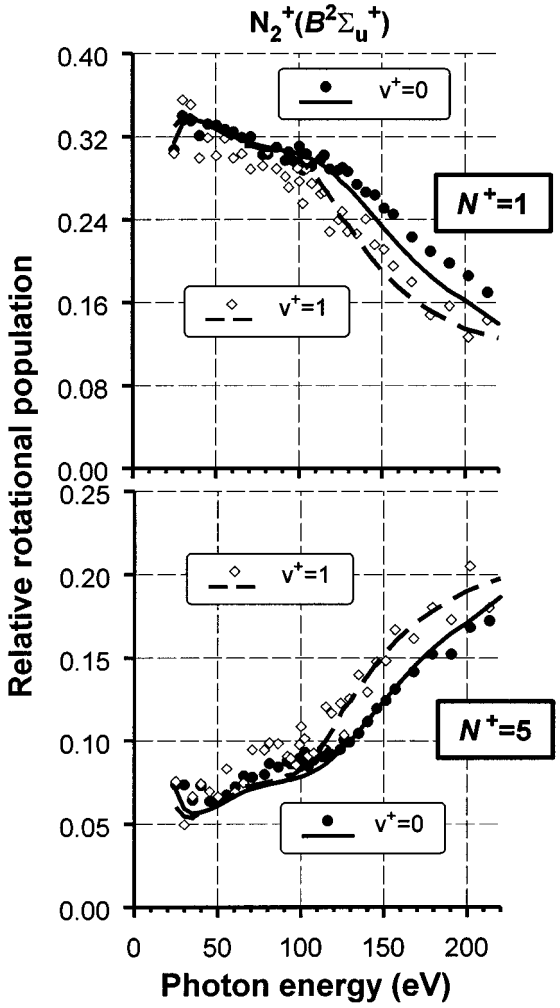

FIG. 3. Comparison of two relative rotational population curves, $N^+=1$ and $N^+=5$, for $v^+=0$ and $v^+=1$.

lation for the $v^+=1$ level. We have not yet determined the origin of this discrepancy, and are investigating possible causes.

A closer look at the results in Figs. 2 and 3 reveals a pattern to the differences in the rotational populations for $v^+=0$ versus $v^+=1$. Starting with the similarities first, the rotational distributions in both vibrational levels change dramatically with photon energy, with the populations of lower rotational levels decreasing, and those of higher rotational levels increasing. This implies that larger ΔN ionizing transitions increase with photon energy, as seen previously for $v^+=0$.[12,13] Such is the case in the rotational distributions following ionization to the $v^+=1$ vibrational level, too, where low ΔN transitions (i.e., $\Delta N=\pm 1$) dominate at lower photon energies, while larger ΔN transitions (i.e., $|\Delta N|\geqslant 3$) grow in importance as the photon energy is increased. This overall trend is accelerated at the inflection point at 120 eV. Thus the two rotational populations largely track one another from the ionization threshold up to $h\nu_{\mathrm{exc}}\approx 100$ eV. It is beyond this point that stark differences in the ion rotational populations for these two vibrational levels are seen. Consider for example the $N^+=1$ and $N^+=5$ populations highlighted in Fig. 3. The inflection point in the relative rotational populations is shifted down to $h\nu_{\mathrm{exc}}\approx 100$ eV for $v^+=1$, from $h\nu_{\mathrm{exc}}\approx 120$ eV for $v^+=0$. In other words, larger ΔN transitions are setting in at lower photon energies for $v^+=1$ than for $v^+=0$. We clearly have a vibrational state dependence in the partitioning of angular momentum between the photoelectron and ion core. While the current differences between $v^+=0$ and $v^+=1$ are subtle, it is possible to amplify the differences by rotationally cooling the target gas more effectively. Such efforts are underway.

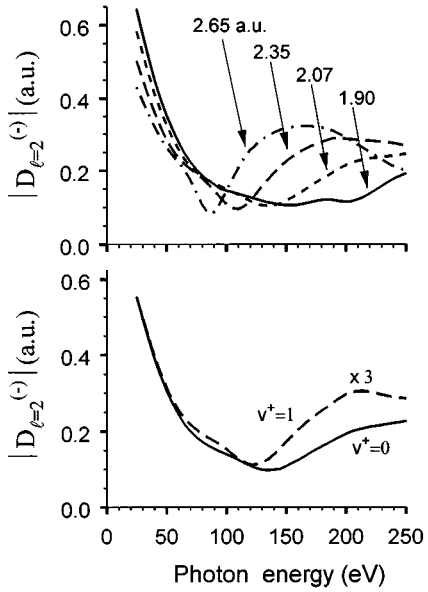

FIG. 4. Calculated $l=2$ partial wave dipole strengths for $2\sigma_u\rightarrow k\sigma_g$ photoionization of N_2. Top frame: calculations for different fixed internuclear separations, illustrating the R-dependence of the Cooper minima. Bottom frame: R-averaged results for ionization to $v^+=1$ compared to $v^+=0$. Note that the split that occurs between the curves at $h\nu_{\mathrm{exc}}\approx 120$ eV mimics the spectral dependence observed in Fig. 3.

To more completely understand and interpret the dynamics of the ionization process, we examine the R-dependence of one of the partial waves contributing to the photoelectron matrix element. In particular, we focus our attention on the $l=2$ wave of the $2\sigma_u\rightarrow k\sigma_g$ continuum, one of the channels which exhibits a Cooper minimum. Plotted in the top frame of Fig. 4 is the calculated dipole strength of this component for different internuclear distances. The broad minimum shows a pronounced shift to lower photon energies with increasing R. In the bottom frame of Fig. 4, the R-averaged results are given for $v^+=0$ and $v^+=1$. The $v^+=1$ curve exhibits a minimum at lower photon energy, which is expected as the R-centroid for ionization to $v^+=1$ is larger than for ionization to $v^+=0$. Thus, ionization to the $v^+=1$ level follows the curves that shifts the Cooper minimum to lower energy. These data allow us to understand the R-dependence of the angular momentum partitioning. This shift leads to a suppression of high-l components[12,13] at a lower photon energy on ionization to the $v^+=1$ level than for ionization to $v^+=0$. Since the $l=2$ component is subse-

quently enhanced at higher energies, large ΔN transitions start to dominate earlier in the photoionization to $v^+=1$. As a result, the ''fork'' observed for the relative rotational populations seen in Fig. 3 at $h\nu_{\mathrm{exc}} \approx 120$ eV tracks the divergence of the vibrationally resolved Cooper minimum shift seen in the bottom frame of Fig. 4. The $k\sigma_g$ $l=4$ component also displays a Cooper minimum. Its behavior is similar to that of $l=2$, and will be discussed in detail elsewhere.[3]

There are two likely causes for the shifting of these Cooper minima,[11,23] which can be distinguished as initial and final state effects. The initial state contribution arises from the variation of the angular momentum composition of the target $2\sigma_u$ orbital with internuclear distance. Because photoionization to alternative photoion vibrational levels has the effect of emphasizing different regions of R, the extent to which a Cooper minimum contributes to the cross section will vary with photoion vibrational level. However, the $2\sigma_u$ orbital composition evolves only slightly over the pertinent range of internuclear separations, indicating that effects in the continuum also contribute to the observations. Specifically, the scattering of the photoelectron into partial waves exhibiting Cooper minima is R-dependent, and is a manifestation of how the molecular potential experienced by the photoelectron mediates the coupling between electronic and photoion angular momenta.[12,13] Both the initial and final state contributions are pertinent to the observed effects, and a more complete discussion will be provided elsewhere.[23]

In conclusion, we have exploited Cooper minima to probe correlations between electronic, vibrational, and rotational motions in $2\sigma_u^{-1}$ photoionization of N_2. The results show clearly that R-dependent Cooper minima lead to a dependence of photoion rotational populations on the photoion vibrational level. Because Cooper minima are ubiquitous in molecular systems,[15] such photoionization studies can be effective probes of vibrational–rotational–electronic correlations. Furthermore, the current study demonstrates the utility of dispersed fluorescence as a survey tool to complement electron spectroscopy. The current investigation also highlights a general theme that emerges from our previous work.[11–13,21,25–27] Specifically, vibrationally and rotationally resolved aspects of molecular photoionization provide a means of ''dissecting'' the angular momentum composition of the electronic continuum and of understanding microscopic aspects of the scattering dynamics, even when the unresolved cross sections are nearly featureless, as is the case in the current study.[23] The key point is that probes which emphasize the molecular nature of the process, such as vibrationally and rotationally resolved methods, are naturally well-suited for elucidating the underlying dynamics.

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